Electronic and Molecular Structures of Poly(hydroxymethylene) and Poly(vinyl alcohol)

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ABSTRACT: The CNDO/2 method using the tight-binding approximation for polymers was applied to poly(hydroxymethylene) (PHM) and poly(vinyl alcohol) (PVA) in several conformations. CNDO/2 calculations were also carried out for the model molecules of PVA. The stability difference estimated experimentally between the isotactic and syndiotactic polymers was reasonably explained by the present calculations. The contribution of hydrogen bonding to the stability of these polymer molecules is discussed.

KEY WORDS Poly(vinyl alcohol) / Poly(hydroxymethylene) / MO
Calculation / CNDO/2 / Conformational Stability /

Poly(hydroxymethylene) (PHM) and poly(vinyl alcohol) (PVA) may be considered as the model molecules of poly(saccharide). Saccharides are very important substances *in vivo*. In animals, saccharides exist, *e.g.*, in glycogen, and in plants they exist, *e.g.*, in cellulose. Thus, it is desirable to know the electronic and molecular structures of poly(saccharide)s. However, poly(saccharide)s have very complex compositions and molecular structures in general. Therefore, we have examined the electronic and molecular structures of PHM and PVA as the model molecules of poly(saccharide)s. Molecular structures, chemical and physical properties of PVA have been very extensively examined up to the present time.¹⁻¹³ However, there are no good solvents for dissolving PHM. Consequently, there are few studies on PHM.^{6,7,14,15} PHM can be considered to have a chemical unit similar to PVA. Accordingly, it is worth mentioning whether there are close relations between the molecular and electronic structures of PHT and PVA.

The electronic structures of polymers have been extensively examined by Imamura and his coworkers.¹⁶⁻¹⁸ The procedure for calculations has already been successfully applied to several linear polymers.¹⁹⁻²⁶ Recently, the MNDO method was

applied for calculating the electronic structure and certain physical properties of polyethylene.²⁷

In the present study, we investigate the electronic structures of PHM and PVA by the CNDO/2 method²⁸ that is based on the tight-binding approximation.²⁹ The CNDO/2 calculations were also carried out for the model molecules of PVA.

The numerical calculations were carried out as in previous papers.^{18,21} The geometries used for the calculations are summarized in Table I. The skeletal conformations for all molecules concerned were assumed to be *trans* zigzag so as to simplify the cal-

Table I. Geometries of PHM and PVA

$r(\text{C-H})$, Å	1.09 ^a
$r(\text{C-O})$, Å	1.40 ^a
$r(\text{C-C})$, Å	1.55 ^a
$r(\text{O-H})$, Å	1.01 ^b
$\phi(\text{CCC})$	109.47122° ^a
$\phi(\text{COH})$	105.937° ^a
$\phi(\text{CCH})$	109.332° ^c
$\phi(\text{CCO})$	110° ^c

^a From ref 30.

^b From ref 31.

^c From ref 21.

Figure 1(a). Structures, atom, and segment numberings of PHM.

Figure 2. Structures of $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ (Model-1), and $\text{CH}_3\text{CH}(\text{OCH}_3)\text{CH}_2\text{CH}(\text{OCH}_3)\text{CH}_3$ (Model-2).

Figure 1(b). Structures, atom, and segment numberings of PVA.

culations. Schematic structures, and atom and segment numberings are shown in Figures 1 and 2.

RESULTS AND DISCUSSION

Poly(hydroxymethylene) (PHM)

Stereochemical study on PHM was carried out extensively by ^{13}C NMR spectroscopy in a previous paper.¹⁵ In that paper, the authors discussed the conformational stability of thirteen rotational isomers. However, in this paper only four typical forms for PHM are dealt with. The total energies calculated are summarized in Table II. The terms intrasegment and intersegment along with their meaning are given in ref 21. The total energies of syndiotactic (Syn) PHM are slightly lower than those of isotactic (Iso) PHM. This implies that Syn

Table II. Total energy (eV) of PHM

Energy	Syn-1	Syn-2	Iso-1	Iso-2
Total	-1477.45	-1477.44	-1477.40	-1477.40
Total intrasegment	-1446.77	-1446.62	-1446.82	-1446.67
Total one center	-1284.48	-1284.46	-1284.53	-1284.57
Total two center	-162.29	-162.16	-162.29	-162.10
Total intersegment	-30.68	-30.82	-30.57	-30.73
Total two center 0-1 ^a	-15.29	-15.35	-15.24	-15.31
0-2	-0.05	-0.05	-0.04	-0.05
0-3		-0.01		-0.01

^a For simplicity, 0-1 (segments) means the central and the first nearest neighbor segments, 0-2, 0-3, ... refers to the central and the second, third, ... nearest neighbor segments. In the present article, upto 0-4 segments were taken consideration for all polymers under study. Energy terms: absolute values less than 0.01 eV are not given. (Energy, see eq. 1-4 of ref 21 for more details.)

Table III. The difference in the two center interaction energy (eV) in the 0-1 segments between Syn-1-PHM and Iso-1-PMA^a

	⁰ C1 ^{b,c}	¹ H2 ^d	¹ O3 ^d	¹ H4	¹ C5	¹ H6	¹ O7	¹ H8	Total
Resonance term									0.04
⁰ C1 ^{b,c}		0.01	-0.01						
⁰ O3			0.01						
⁰ C5	0.01	0.01	-0.01						
⁰ H6 ^d	0.01	-0.04	0.03		0.01				
⁰ O7 ^d	-0.01	0.04	-0.02						
⁰ H8		-0.01							
Exchange term									0.00
⁰ H6		-0.01	0.01						
⁰ O7		0.01	-0.01						
Electrostatic term									0.01
⁰ H2			-0.01						
⁰ O3		-0.01	0.01				-0.01	0.01	
⁰ H4							0.01		
⁰ H6							-0.01		
⁰ O7			-0.05	0.04		-0.01	0.01		
⁰ H8			0.04	-0.03					
Total									0.05

^a Digits show energy difference: (Iso-1-PHM) - (Syn-1-PHM). Enery terms: absolute values less than 0.01 eV are not given. (See eq 4 of ref 21 for more details.)

^b Atom numberings are show in Figure 1(a).

^c For example, (⁰C1, ¹C1) refers to the interaction element between the C1 carbon atom in the central segment and the C1 carbon atom in the first nearest neighbor segment.

^d Distance Syn-1; (⁰O7 ... ¹H2)=3.34 Å, (⁰H6 ... ¹O3)=3.35 Å,
 (⁰H6 ... ¹H2)=2.50 Å, (⁰O7 ... ¹O3)=2.82 Å;
 Iso-1; (⁰O7 ... ¹H2)=2.66 Å, (⁰H6 ... ¹O3)=2.68 Å,
 (⁰H6 ... ¹H2)=3.07 Å, (⁰O7 ... ¹O3)=3.63 Å.

PHM is more stable than the Iso PHM. It is well known that the OH groups of PHM are only somewhat acetylated under ordinary conditions.^{7,14}

This implies that PHM ordinarily is likely to exist predominantly in the Syn form. Thus, in the Syn form, once a fairly bulky group of CH₃CO is

introduced into the main molecular chain, it becomes more difficult for acetylation to follow.

A comparison was made of the energies of Syn-1 and Iso-1. The total intrasegment energy of Iso-1 was found to be smaller than Syn-1. On the other hand, in the total intersegment energy, the reverse is true. This same situation is also shown for Syn-2 and Iso-2. In the total intrasegment energy, the energy difference appears in the one center term. In the total intersegment energy, the difference appears in the 0-1 segments.

Let us examine the difference in detail using Table III. Fairly large values appeared in the resonance and electrostatic terms. However, the elements that appeared in the electrostatic term nearly cancel each other out. The resonance term is responsible for the total difference. In this term, ($^0\text{O}7$, $^1\text{H}2$) and ($^0\text{H}6$, $^1\text{O}3$) stabilize the Syn form, and ($^0\text{H}6$, $^1\text{H}2$) and ($^0\text{O}7$, $^1\text{O}3$) stabilize the Iso form. The relation ($^0\text{O}7 \dots ^1\text{H}2$) or ($^0\text{H}6 \dots ^1\text{O}3$) in Syn-1 is *trans*, but these are *gauche* in Iso-1. The relation ($^0\text{H}6 \dots ^1\text{H}2$) or ($^0\text{O}7 \dots ^1\text{O}3$) in Iso-1 is *trans*, but *gauche* in Syn-1. In the *trans* state, the distances between these atoms are greater than those in the *gauche* state. The *trans* interaction stabilizes the form, but the *gauche* interaction destabilizes it. These *trans-gauche* interactions are the dominant factors

for the conformational stability of Iso and Syn PHM. This is one important finding in the present work.

Table IV. The difference in the two center interaction energy (eV) in the central segment between Syn-1-PHM and Syn-2-PHM^a

	C1 ^b	H2	O3	H4	Total
Resonance term					0.07
			Symmetric		
C5 ^b	-0.02	-0.01	-0.06	0.16	
O7				-0.02	
Exchange term					-0.01
			Symmetric		
H4			0.01		
C5	-0.02				
Electrostatic					0.07
			Symmetric		
C5				0.08	
O7				-0.07	
H8				0.05	
Total					0.13

^a Digits show energy difference: (Syn-2-PHM) - (Syn-1-PHM). Energy terms: absolute value less than 0.01 eV are not given. (See eq 3 of ref 21 for more details.)

^b See footnote b of Table III.

Table V. The difference in the two center interaction energy (eV) in the 0-1 segments between Syn-1-PHM and Syn-2-PHM^a

	$^1\text{C}1^{b,c}$	$^1\text{O}3$	$^1\text{H}4$	$^1\text{C}5$	$^1\text{O}7$	$^1\text{H}8$	Total
Resonance term							-0.07
$^0\text{C}1^{b,c}$		-0.01	0.08				
$^0\text{O}3$	0.02		0.93				
$^0\text{H}4$	-0.10	-0.95	-0.08				
$^0\text{C}5$	0.01	0.03					
Exchange term							0.01
$^0\text{O}3$			0.08				
$^0\text{H}4$		-0.08					
Electrostatic term							0.00
$^0\text{C}1$			-0.05				
$^0\text{O}3$			-0.13				
$^0\text{H}4$	0.06	0.14		0.01	-0.03	0.02	
$^0\text{C}5$			-0.04				
$^0\text{C}7$			0.03				
Total							-0.06

^a See footnote a of Table IV. (See eq 4 of ref 21 for more details.)

^b See footnote b of Table IV.

^c See footnote c of Table III.

As for Syn-1 and Syn-2, Syn-1 is slightly more stable than Syn-2, but Iso-1 and Iso-2 have nearly the same total energy. The Iso-1 and Syn-2 forms are lower in energy than Iso-2 and Syn-2 in the intrasegment, while the reverse is true in the intersegment (see Table II).

Using Tables IV and V, we now discuss the difference between the two center energies of Syn-1 and Syn-2 PHM in some detail. From Table IV, we can recognize that the energy difference between the intrasegment two center terms owes mainly to the element of (C5, H4) in the resonance term. The distance (C5...H4) in Syn-1 is 3.21 Å, and that in Syn-2, 2.32 Å. The group H4-O3-C1-C5 is *trans* in Syn-1, but it is *gauche* in Syn-2. Therefore, the *trans* interaction of H4...C5 stabilizes the Syn-1 form. The same interaction was shown in the previous paragraph. The next dominant elements exist in the electrostatic term. The same situation is also seen in the Iso-1 and Iso-2 PHM.

With the 0-1 interaction terms as shown in Table V, the energy difference between Syn-1 and Syn-2 PHM appears in each term. However, the elements in the exchange and electrostatic terms nearly cancel each other out. Thus, the resonance term remains. Here, the elements ($^0\text{H4}$, $^1\text{O3}$) and ($^0\text{O3}$, $^1\text{H4}$) and the elements ($^0\text{H4}$, $^1\text{C1}$) and ($^0\text{C1}$, $^1\text{H4}$) cancel each other out. In other words, the former elements stabilize the Syn-2 form, more while the latter elements stabilize the Syn-1 form more than the Syn-2 form. It is thus noticed that the element ($^0\text{H4}$, $^1\text{H4}$) is the dominant one for determining the energy difference in the intersegment term. The same is also true for Iso-1 and Iso-2 PHM.

From these calculations, it can be seen that the elements (C5, H4), ($^0\text{O7}$, $^1\text{H2}$), ($^0\text{H6}$, $^1\text{O3}$), ($^0\text{H6}$, $^1\text{H2}$), ($^0\text{O7}$, $^1\text{O3}$), and ($^0\text{H4}$, $^1\text{H4}$) govern the conformational stability of PTM. This is the major finding of the present work. However, the energy difference between, *e.g.*, Iso and Syn, is not large enough to rule out the existence of the Iso form.

Poly(vinyl alcohol) (PVA)

All calculated energies are shown in Table VI. These calculations were carried out on the Iso and Syn species. The total energy of Iso PVA was found to be smaller than that of Syn PVA. The total intrasegment energy is smaller in Syn than in Iso, while the total intersegment energy is smaller in Iso than in Syn. Within the total intrasegment energy,

Table VI. Total energy (eV) of PVA

Energy	Iso	Syn
Total	-1950.17	-1949.58
Total intrasegment	-1920.45	-1921.12
Total one center	-1619.68	-1620.78
Total two center	-300.77	-300.34
Total intersegment	-29.71	-28.46
Total two center 0-1 ^a	-14.85	-14.22

^a See footnote a of Table II. (Energy, see eq 1-4 of ref 21 for more details.)

the greater part of the energy difference between the two species appears in the one center term. In the total intersegment energy, the difference in the energy between the two species appears in the 0-1 segments.

We now turn to a discussion of the origin of these energy differences using Tables VII and VIII. At first, we discuss the intrasegment energy (see Table VII). The resonance and the electrostatic terms stabilize the Iso form more than the Syn form. On the other hand, the exchange term destabilizes the Iso form more than the Syn form. Among the elements, (O10, H4) contributes the most in determining the energy difference.

In the intersegment 0-1 term, most part of the energy difference appears in the resonance term. The largest element to determine the energy difference between Iso and Syn is ($^0\text{H11}$, $^1\text{O3}$). The role played by the element ($^0\text{H11}$, $^1\text{O3}$) is the same as that of (O10, H4) discussed in the preceding paragraph. The distance ($^0\text{H11} \dots ^1\text{O3}$) or (O10...H4) is 1.58 Å in the Iso form, and is 2.94 Å in the Syn form. For the Iso form, the distance is suitable for hydrogen bonding. However, in the case of the Syn form, it is too large to allow for hydrogen bonding.

From an examination of the calculated results, we notice that the conformational stability of PVA is largely affected by the hydrogen bonding of the intrasegment as well as the intersegment terms. This differs from the situation of PHM, and is considered to be of interest.

The crystal structure of PVA was proposed by Bunn in 1948² and was further studied by Nitta *et al.*³ Iso PVA was also studied by X-ray analysis, and a model for it was proposed in 1962.⁴ The sheet structure was commented on in a recent paper.¹² On the other hand, the lattice parameters of monoclinic

Table VII. The difference in the two center interaction energy (eV) in the central segment between Iso PVA and Syn PVA^a

	C1 ^b	O3	H4	C8	O10	Total
Resonance term						0.59
O3 ^b	−0.12		Symmetric			
H4		−0.39				
H9			−0.29			
O10		−0.24	1.91	−0.12		
H11					−0.39	
Exchange term						−0.44
H4		−0.36	Symmetric			
O10			0.18			
H11					−0.36	
Electrostatic						0.27
H4		0.29	Symmetric			
H9			0.12			
O10		−0.24	−0.20			
H11		0.12	−0.14		0.29	
Total						0.42

^a Digits show energy difference: (Syn PVA)−(Iso PVA). Energy terms: absolute values less than 0.01 eV are not given.

(See eq 3 ref 21 for more details.)

^b Atom numberings are shown in Figure 1(b).

Table VIII. The difference in the two center interaction energy (eV) in the central segment between Iso-PVA and Syn-PVA^a

	¹ H2 ^{b,c}	¹ O3	¹ H4	Total
Resonance term				0.69
⁰ O10 ^{b,c}		−0.12		
⁰ H11	−0.14	0.95		
Exchange term				0.10
⁰ H11		0.09		
Electrostatic term				−0.17
⁰ O10		−0.12	0.06	
⁰ H11	0.06	−0.10	−0.07	
Total				0.63

^a See footnote a of Table VII. (See eq 4 of ref 21 for more details.)

^b See footnote b of Table VII.

^c See footnote c of Table III.

and orthorhombic PVA were reported in 1974.⁸ Ito *et al.*¹² concluded that among the crystal structures the sheet structure is better than Bunn's model.⁴

In the present work, we treat only the single polymer chain. A similar calculation concerning two, polymer chains will be reported elsewhere.

Model Molecules

In order to study the energy difference appearing in polymers, calculations on model molecules were carried out for PVA. The results are shown in Table IX. Energy partitioning was made according to ref 21. At this point, we take up four models having the same geometries as the polymer. In the OH species (Model-1), the Iso form is slightly more stable than the Syn form. However in the OCH₃ species (Model-2), the Syn form is more stable than the Iso form. In Model-1, the steric repulsion between adjacent O–H groups may not be very strong. However, in Model-2, the repulsion between the substituted groups in the Iso form may be larger than in the Syn form (see two center electrostatic term). Mynderse *et al.*³² obtained isotactic polymethoxy-1-alkanes from natural plants. Thus, in this case it may be said that isotactic alkanes can be naturally synthesized under special conditions.

From this, we can recognize that, in the Model-1,

Table IX. Total energy^a (eV) of CH₃CH(OH)CH₂CH(OH)CH₃ (Model-1) and CH₃CH(OCH₃)CH₂CH(OCH₃)CH₃ (Model-2)

Energy	Model-1		Model-2	
	Iso	Syn	Iso	Syn
Total	-81.77	-81.76	-98.95	-99.11
Total one center	-66.63	-66.65	-78.94	-78.93
Total core	-117.16	-117.02	-137.66	-137.59
Total electron repulsion	50.53	50.37	58.71	58.66
Total two center	-15.14	-15.12	-20.00	-20.18
Total resonance	-15.41	-15.37	-20.58	-20.56
Total exchange	-3.63	-3.63	-4.82	-4.82
Total electrostatic	3.89	3.89	5.40	5.20

^a See eq 7—9 of ref 21 for more details.

the Iso form becomes more stable than the Syn form as a result of forming selective hydrogen bonds. This is seen in the case of actual polymers.

In the present paper, the main chain of the polymer is assumed to be completely *trans*. For other skeletal conformations, the treatment will be carried out in future work.

CONCLUSIONS

The relative stability of the four species of PHM and that of the two species of PVA are reasonably explained by the CNDO/2 calculations based on the tight-binding approximation.

From these calculations it was found that hydrogen bonding plays an important role in the conformational stability of PVA but not in that of PHM. This is the most important conclusion derived from the present work, and implies that the configurational stability of poly(saccharides) skeletal rings can be determined partly by hydrogen bonding. Another major factor governing the stability may be the *trans-gauche* interaction (see text for more details).

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